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Equipment for processing and characterizing polymers was purchased with this DURIP equipment grant. Three items were purchased. The Reactive Ion Etching Unit (RIE) was purchased as an add-on to an existing instrument and the installation was completed in March 98. It will be used for making ridge waveguides in polymers. The high temperature poling station that was purchased is now being used by three separate researchers to pole a variety of polymers for parametric mixing devices.  The single crystal growing apparatus was installed almost immediately and has been very successful in making state-of-the-art single crystal polydiacetylene PTS crystals. It has been demonstrated that these crystals have damage thresholds of > 400 GW/cm² for 100 femtosecond pulses in the communications band at 1550 nm. In these crystals, the strongest reported multi-photon absorption ever, three and four photon, has been observed. Single crystal films for waveguiding have been grown and slab and channel waveguides in PTS have been demonstrated.			
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# Progress (and Final) Report:

#### 1. Proposal Abstract:

The proposed instrumentation is critically needed for the processing and characterization of poled polymer and organic single crystal film waveguides for a variety of photonics applications. The instrumentation requested and listed below includes both commercial units and equipment to be assembled from parts:

- (1) A polymer poling station for operation at >250°C in a controlled environment;
- (2) A reactive-ion-etching station module for channel waveguide fabrication,
- (3) A single crystal, PTS film growth apparatus;
- (4) A near-infrared polarized microscope for assessing PTS film quality.

Our overall program goal is to demonstrate that polymers are superior materials for nonlinear photonics applications involving frequency conversion. We are investigating the suitability of poled polymer waveguides for second order nonlinear interactions and have achieved values for second harmonic generation (SHG) in DANS which are competitive with state-of-the-art LiNbO<sub>3</sub> channel waveguides in the 1550 nm communications band. However, the material used, DANS, has too many drawbacks. "Optimer", developed by ROITECH, has nonlinearities superior to those of DANS as well as vastly improved properties in terms of losses, thermal stability and photosensitivity. The first two items listed above are required for (1) poling this material at temperatures >250°C in inert atmospheres, and (2) forming channel waveguides by reactive ion-etching.

The second project is aimed at using "bright" spatial solitons for reconfigurable interconnects in the single crystal polymer polydiacetylene para-Toluene Sulfonate (PTS). At 1550 nm this material has ideal nonlinear optical properties for spatial soliton propagation in planar waveguides at watt optical power levels. Thin film, single crystal, polymer waveguides need to be fabricated. The growth equipment (3) requested will be used to grow such thin film waveguides. The near-infrared polarized microscope (4) will allow us examine film quality for this material which is highly absorbing in the visible.

# 2. Equipment Purchased:

- #1 <u>High Temperature Poling Station</u>:
  Micromanipulator: Model #D6-V1 which includes the HSM 6" diameter heater stage
- #2 Reactive Ion Etching Secondary Module (option to be added to existing Plasma Enhanced Chemical Vapour Deposition System)

  Model #790, including chamber, mass flow controllers, power supply
- #3 Single Crystal Thin Film Growth Apparatus, consisting of miscellaneous items

It was also proposed to purchase an IR Polarized Microscope. However, increases in the prices for the above items over the one year period between proposal and purchase did not leave enough funds to purchase the microscope.

# 3.0 Resulting Research Activity

# 3.1 <u>High Temperature Poling Station</u>:

This unit was purchased, delivered and installed in our cleanroom by the end of 1998. It is currently under heavy use for poling polymers for applications to second harmonic generation by three different researchers in the Stegeman group.

#### 3.2 Reactive Ion Etching Secondary Module:

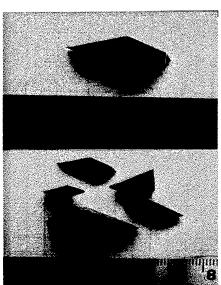
This unit was purchased, delivered and installed by March 1998. The installation took longer than anticipated because a separate gas handling system for the RIE had to be installed and approved. The system is finally operational and the learning curve for etching polymers has been initiated.

# 3.3 Single Crystal Growth Apparatus:

This apparatus was purchased and was operational within a month. It was used to fabricate single crystal PTS, both in bulk and thin film form with excellent success.

## 3.3.1 Bulk PTS Crystals

A number of experiments were made possible by the fabrication with the equipment purchased of optical quality PTS crystals at CREOL. We found that it is relatively straightforward to grow optical quality PTS in its monomer form. However, on polymerization, the crystal contracts by a few percent creating large strains along one of its axes leading to defects and cracking. Our approach has been to control the polymerization process by slowing it



down by two orders of magnitude during the period from 10% to 90% polymerization. This allows some annealing of the stresses and we have made crystals 100 microns to a few mm thick, up to 1 cm wide and a few cms long, see Fig. 1. The optical quality of these crystals was very good, as evidenced by the very high damage thresholds for 100 fsec pulses, and the quality of the z-scans obtained when characterizing the nonlinear properties of the material.

No crystals have been damaged in any Z-scan measurements with 100 fsec pulses at intensities up to 200 GW/cm<sup>2</sup>. This is better than that obtained with semiconductors, and is comparable to the best damageresistant dielectrics such as fused silica. Experiments have been performed at 400 GW/cm<sup>2</sup>, without damage, but were discontinued because the net absorption was too large for meaningful measurements.

With these crystals we have made some breakthroughs Figure 1 PTS single crystals in our research on the nonlinear optical properties of PTS (bisparatoluene sulfonate) single crystals. Our previous work on these conjugated polymers had

established that they had exceptionally large third order nonlinear properties. Specifically, there is a large (compared to other materials) two photon absorption coefficient from about 700 nm to 1300 nm, with a huge peak at 920 nm of >800 cm/GW. Furthermore the non-resonant nonlinear refractive index coefficient is the largest known,  $2x10^{-12}$  cm<sup>2</sup>/W. These remarkable nonlinear properties make this material ideal for applications to optical limiting, all-optical switching and demultiplexing and reconfigurable interconnects based on spatial solitons (which we have also recently observed in PTS).

In the non-absorbing region of the spectrum (at 1600nm) we have now observed very large three and four photon absorption. The intensity-dependent absorption coefficient has the form here  $\Delta\alpha = \alpha_3 I^2 + \alpha_4 I^3$  where  $\alpha_3$  and  $\alpha_4$  are the three and four photon absorption coefficients respectively. We measured  $\alpha_3 = 0.13 \pm 0.08$  cm<sup>3</sup>/GW<sup>2</sup> and  $\alpha_4 = 0.016 \pm 0.03$  cm<sup>5</sup>/GW<sup>3</sup>. Previous observations of four photon absorption (in semiconductors) are still in dispute and this is certainly the first observation in a non-semiconducting material. The four photon coefficient is orders of magnitude larger than reported in any semiconducting material. The significance of four photon absorption is that a doubling of the intensity leads to a factor of eight increase in the absorption coefficient (and the transmission is proportional to exp[- $\alpha$ z]) so that a material essentially becomes opaque with small intensity changes.

Three photon absorption has been observed in a number of materials before, including organic materials. The magnitude of the three photon coefficient far surpasses all previous reports in any material.

Very recently the experiments were extended to 1860 nm where we expect a peak in the three and four photon coefficients. In fact, an order of magnitude increase in the four photon absorption coefficient (over the 1600 nm value) to  $0.2~{\rm cm}^5/{\rm GW}^3$  was measured. This means that at intensities of just a few GW/cm², the net nonlinear absorption is larger than two photon absorption in most organic materials. We could not go to low enough intensities to measure the three photon coefficient because of the limited sensitivity of our detector at these wavelengths. Further experiments on  $\alpha_4$  are underway at other wavelengths.

# 3.3.2 Thin Film PTS Crystal Waveguides

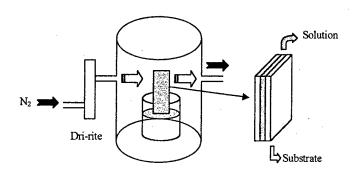


Figure 2 Apparatus for growing thin PTS films.

We have developed a technologically simple and highly reproducible fabrication method based on capillary action, slow solvent evaporation and controlled polymerization for making PTS channel waveguides for all-optical devices. A monomer PTS single crystal film was grown by slow solvent evaporation, as shown in Fig. 2. The growth procedure can be briefly described as follows. The PTS-acetone solution with concentration around 0.4g/ml was

pulled into the gap between a pair of precleaned glass substrates by capillary action. The thickness of the grown film thickness was determined by the plate separation. This substrate-solution-substrate assembly was put into a dessicator with controllable nitrogen flow to achieve slow solvent evaporation, thus yielding PTS crystal films with typically 20-30mm<sup>2</sup> surface area and 0.5-3µm thickness. The as-grown PTS monomer film was polymerized by annealing in nitrogen at 55°C for 200 hours.

Because the single crystal PTS film is believed to be chemically inert, we expected that photolithographic processing of the polymer PTS crystal film wouldn't damage the film itself.

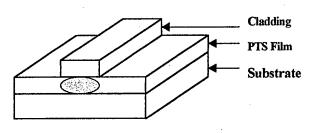
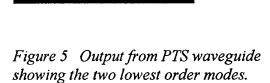


Figure 3 PTS channel waveguide structure

We fabricated a stripe-loaded structure on top of the PTS film by adopting standard photolithography techniques. Fig. 3 shows the structure of a PTS channel waveguide. The top cladding layer is a low index (1.64) material. Compared with the high index of PTS which is 1.88 at 1.6 µm, this cladding ridge is sufficient to confine a laser beam inside the PTS film under the channel. Fig. 4 is the output image of a

laser beam after passing through this stripe-loaded structure,
excited at the input facet by end fire coupling. It clearly shows the
two lowest order channel waveguide modes, i.e. the input laser
bean was confined two-dimensionally to yield an elliptical beam
output by channel waveguiding. Because the chemical properties
of PTS are compatible with standard growth and photolithographic
patterning techniques, these results should facilitate the fabrication
of the complex channel waveguide structures needed for all-optical
switching.



# Refereed Papers:

1. H. Shim, M. Liu, C. Hwangbo and G.I. Stegeman, "Four Photon Absorption in the Single Crystal Polymer Bis-Paratoluene Sulfonate", Opt. Lett., 23:430-2 (1998)

## **Conference Presentations:**

- 1. M. Liu, C.K. Hwangbo, L. Friedrich and G.I. Stegeman, "Preparation and Characterization of Single Crystal PTS Waveguide Film", OSA/ACS Joint Topical Meeting on Organic Thin Films for Photonics Applications, Long Beach, October 1997, paper WC2, pp35-36
- 2. "Four Photon Absorption in the Single Crystal Polymer PTS", (postdeadline paper), OSA/ACS Joint Topical Meeting on Organic Thin Films for Photonics Applications, Long Beach, October 1997
- 3. M. Liu, L. Friedrich and G. I. Stegeman, "Fabrication of Single Crystal PTS Channel Waveguide", Digest of CLEO'98, (Optical Society of America, Washington, 1998) San Francisco, May 1998, paper CWA2
- 4. Hoon Shim, Mingguo Liu and George Stegeman, "Three and Four Photon Absorption in the Single Crystal Polymer PTS", Digest of CLEO'98, (Optical Society of America, Washington, 1998) San Francisco, May 1998, paper QTuC5
- 5. Hoon Shim, Mingguo Liu, Chang Hwangbo and George I. Stegeman, "Multi-Photon Effects in the Single Crystal Polymer Bis-Paratoluene Sulfonate (PTS) at Ultra High Intensities", invited paper, 8'th Iketani Conference and ICONO4, Hokkaido Japan, October 1998